

Studies of the Light Hydrocarbon Fuel from Waste Polymer Mix

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ABSTRACT: The municipal solid waste become one of the key problem, the world is facing today. Out of this 20% of the solid waste is of polymer waste. These wastes generally comprises of the waste polyethylene such as LDPE, LLDPE, MDPE and HDPE type polyethylene, polypropylene, polyethylene tetra phthalate, polyvinyl chloride polystyrene, PMMA etc. The aim of this paper is to study and to convert the waste municipal solid polymer waste into useful hydrocarbon products. The polymers having polyolefin are very useful materials with different applications, but are reluctant to degradation or deterioration. This causes accumulation of these materials in the environment and hence causing environmental related problems such as infertility of land, sewage problem such as choking of the water bodies etc. The paper studies the scope of the conversion of these non-biodegradable materials into useful light hydrocarbon products. The chromatographic study of the pyrogas and the liquid products from these waste materials were studied. The different chemical reactions followed and there implications were also studied. Different chromatographic study of gaseous and the liquid products also produce evidence of production of some alternative and environmentally sustainable source of energy for our future generations.

KEYWORDS : waste polyethylene, hydrolysis, chromatography

I. INTRODUCTION

Polyethylene are commodity materials which are one of our part and parcel of our life. It finds application in our household items such as packaging, ropes, pipes, medical equipments, poly bags etc. These materials are not easily degraded even by the microorganisms and hence become one of the major threats to the environment. Some other type of polymers such as polyethylene tetra phthalate have oxygen, polyvinyl chloride have chlorine which are also harmful for the environment. Polyolefin's are the saturated polymers have a broad range of applications. Polypropylene and polyethylene are the most widely used polymers. These polyethylene's such as Low density polyethylene (LDPE), Linear low density polyethylene (LLDPE) and High Density Polyethylene (HDPE), ethyl vinyl acetate (EVA) and Polyolefinic elastomers(POE) are generally linear or cross linked in nature. These cross linked polymers are insoluble and forms three dimensional network structures. Due to this cross linking of polyethylene materials it forms a dense network of high molecular weight structure which further improves its impact strength, crack resistance, creep and abrasion resistance without any influence in density and tensile strength. In this paper the thermal conversion of the waste polyethylene's and other polymers into gaseous and liquid hydrocarbon fuels were studied and investigated. Depolymerization of the polyethylene materials breaks the weakly bonded main chain and successively splits monomers at there chain ends. Thermal cracking eliminates a side chain of lower bond dissociation in a plastic of the carbonization residue type. Thermal cracking then causes decomposition, cyclization and other secondary reactions of the plastic and carbonize all of its molecules.[1] The extraction of the lighter hydrocarbon fuel ranging from C1-C4 and C5-C12 hydrocarbon fuel is being estimated and studied. The hydrolytic depolymerization of these waste polymer materials favors higher rate of conversion into useful oil. The gaseous hydrocarbon fuels generated by such degradation process have high calorific value.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 3, March 2016

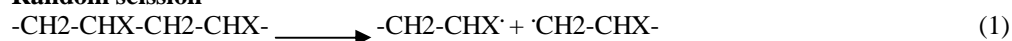
II. METHODOLOGY AND EXPERIMENTATION

The waste polyethylene contains different types of the organic, inorganic and biological residues which are present in the form of contamination. The waste polyethylene is very difficult to treat because of its complex nature and composition. The process of the degradation followed in the process is the hydrolysis process. To carry out this process the polyethylene waste is pyrolysed in a batch reactor and the product is recovered using chilled demineralized water. The product gases were quenched on the surface of the water resulting in the formation of the gaseous and liquid products.

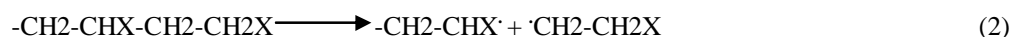
The long chain complex hydrocarbon chain breaks down into short chain molecules. In order to produce and obtain different categories of liquid products the thermal degradation process is upgraded to fractional distillation process. Fractional distillation process is basically thermal degradation except the heat applied is divided into different groups based on specific temperature.[2] Fractional distillations of these chains are divided into different groups based on the type of liquid produced. The gaseous product range from C1-C4 carbon number and the naphtha component carbon chain is in the range of C5-C15. The degradation generally accompanied with free radical chain reaction. When free radicals react with hydrocarbons, some new free radicals and hydrocarbons were produced. In free radical mechanisms, the degradation of polymers generally involves the stages of initiation, propagation, chain transfer and termination. Initiation is the slowest reaction stage and generates macro radicals by chain scission or end-chain breaking of the macromolecular backbone or by scission of the bonds with the pendant groups. The reactivity of the macro radicals, the R-CH₂· radical has a higher reactivity than the R₂CH· and the mobility of the hydrogen atoms in the backbone, the tertiary hydrogen is more reactive than the secondary and primary one which strongly affects the mechanism of polymer degradation and decomposition.[3]. The polyethylene degradation mechanism is followed by random scission, end chain scission, de-propagation, intermolecular and intramolecular hydrogen transfer β-scission, formation of branches and finally termination, either by bimolecular coupling or disproportionation reaction.

i) Initiation:-

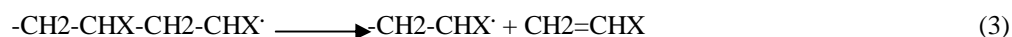
Random scission



End chain scission

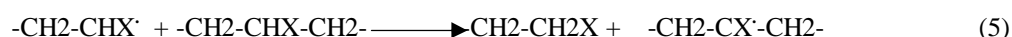
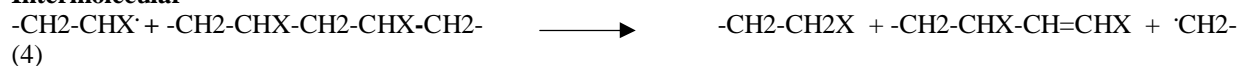


ii) De-propagation



Hydrogen Chain Transfer

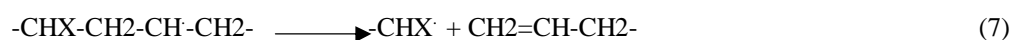
Intermolecular



Intramolecular



β-Cleavage

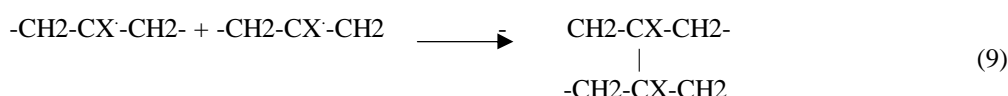
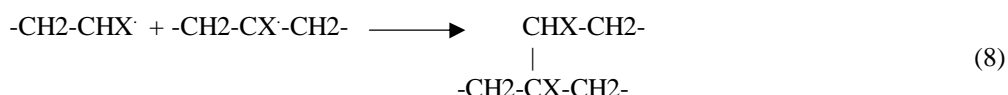


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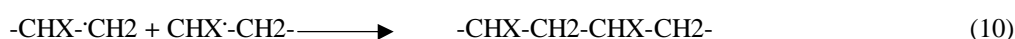
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Formation of Branches



iii) Termination

Bimolecular coupling

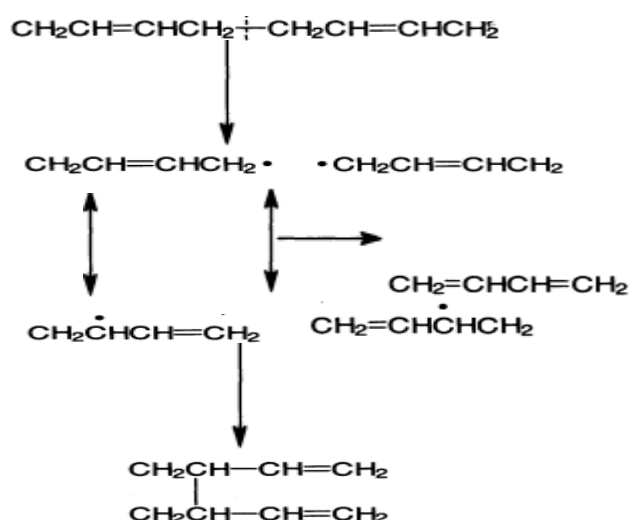


Disproportionation



In case of the polystyrene and its terpolymer acrylonitrile-butadiene-styrene, the degradation begins at some higher temperature say at 300⁰C and above. The observed products are styrene and its oligomers along with some benzene and toluene. In this case at higher temperature the aromatics intensity decreases considerably, but the butadiene remains strong throughout the course of degradation.

The formation of the monomer and the cross linking from degradation of polybutadiene is described in the reactions below.



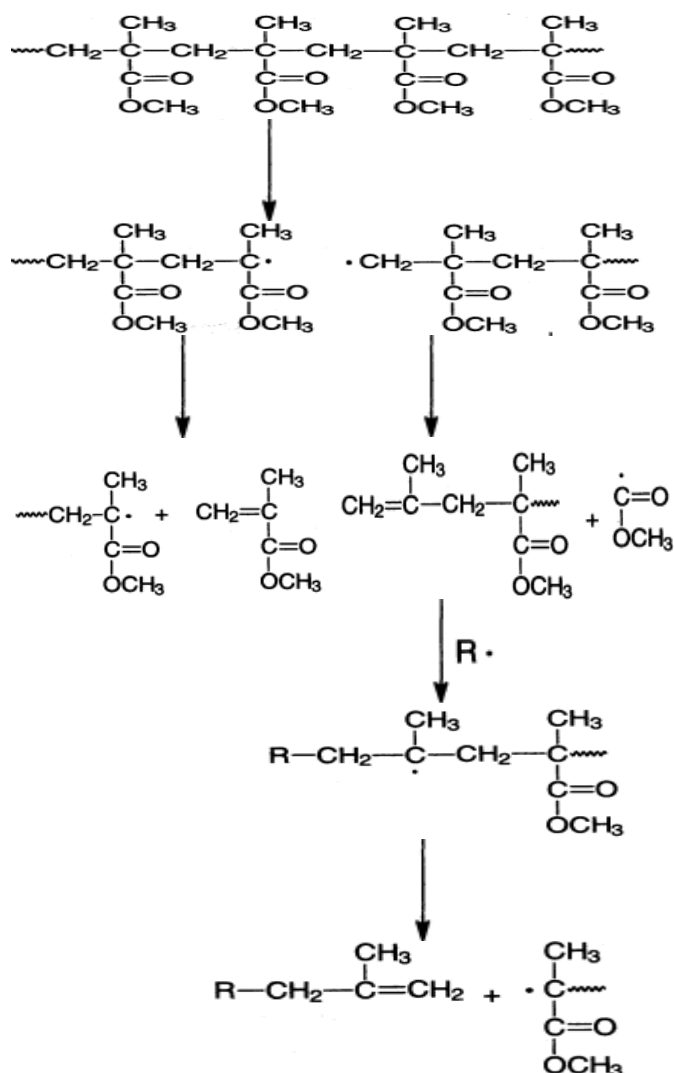
the degradation of the poly(meth) acrylates gives essentially monomers. The degradation of PMMA occurs in two stages. In the first stage water is lost and the poly (methacrylic anhydride) is formed. This occurs at temperature around 130⁰C – 250⁰C. In the second stage the degradation of the polymethacryl anhydride occurs at about 300⁰C - 450⁰C.

The degradation produces monomers, there corresponding isobutyrate, carbonates, oxides, carbon dioxide and some volatiles which have some ketones and aldehydic groups.

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The different products recovered by the thermal hydrolytic depolymerization of the waste polymers have some light component and some heavier components. The light component comprises of the gaseous products and the liquid lighter hydrocarbon, naphtha like products. The gas chromatographic study of the gaseous product is investigated which range from C1-C5 along with some C6 components, hydrogen, CO₂ and traces of CO.

Hydrocarbon types	Components	Concentration V/V %
	H2	11.3
C1	Methane	15.3
C2	Ethane	15.7
	Ethylene	10.7
C3	Propane	13.7
	Propylene	16.2
C4	Propadiene	0.1
	Iso-Butane	0.1
	N-Butane	3.4
	Trans-2 Butene	0.2
	1- Butene	3.2
	Iso-butylene	0.8
	Cis-2-Butene	0.3
C5	Iso-pentane	0.2
	N-pentane	0.5
C6	C6 components	0.5
	CO2	7.8

Table 1. Gaseous component derived from waste polyethylene mix.

The chromatographic study was carried out using RGA analyzer having porapak Q, molecular sieve packed column and plot alumina capillary column. The temperature programming is done for such analysis with ramp temperature of 5°C /min [4][5].

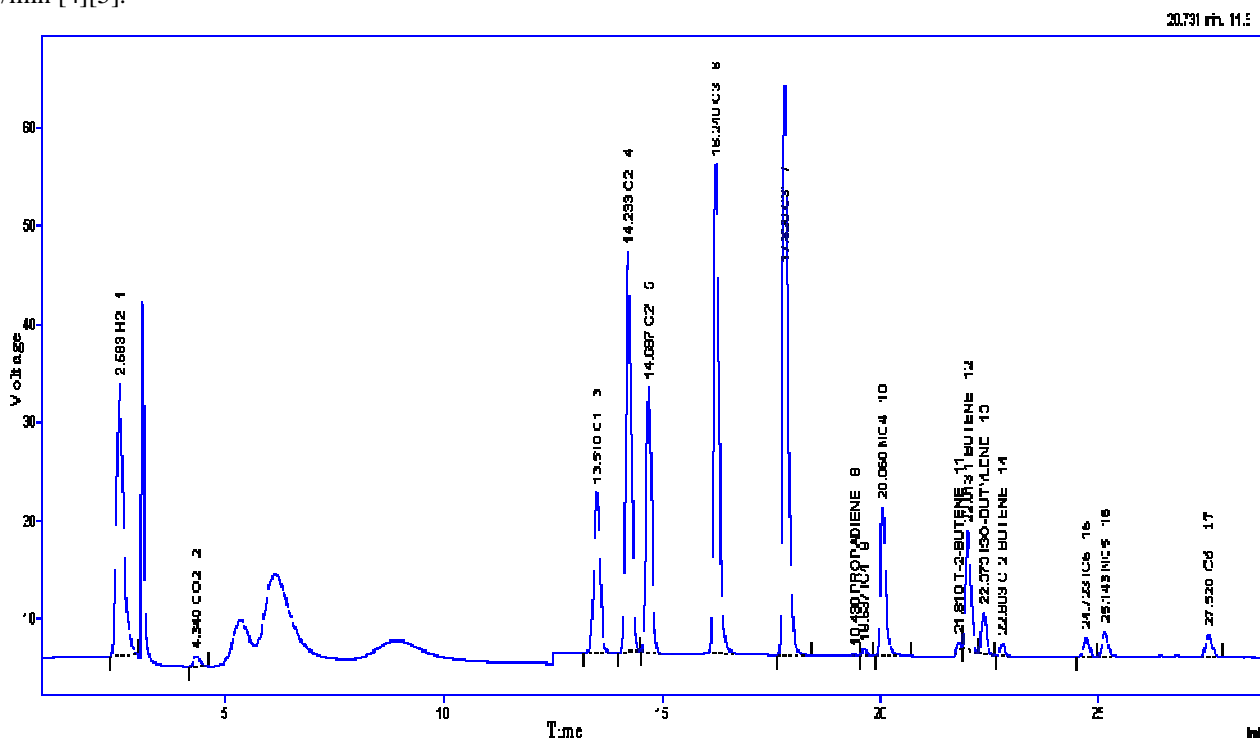


Figure 1. Chromatographic study of the gaseous sample recovered from hydrolytic depolymerization of polyethylene mix.

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The above figure describes the different components recovered from the gaseous components recovered from the degradation of the polyethylene mix. The chromatogram is represented in the form of voltage versus time. On the basis of the different peaks observed at different retention time the components were identified and the concentration were observed which is described in table 1.

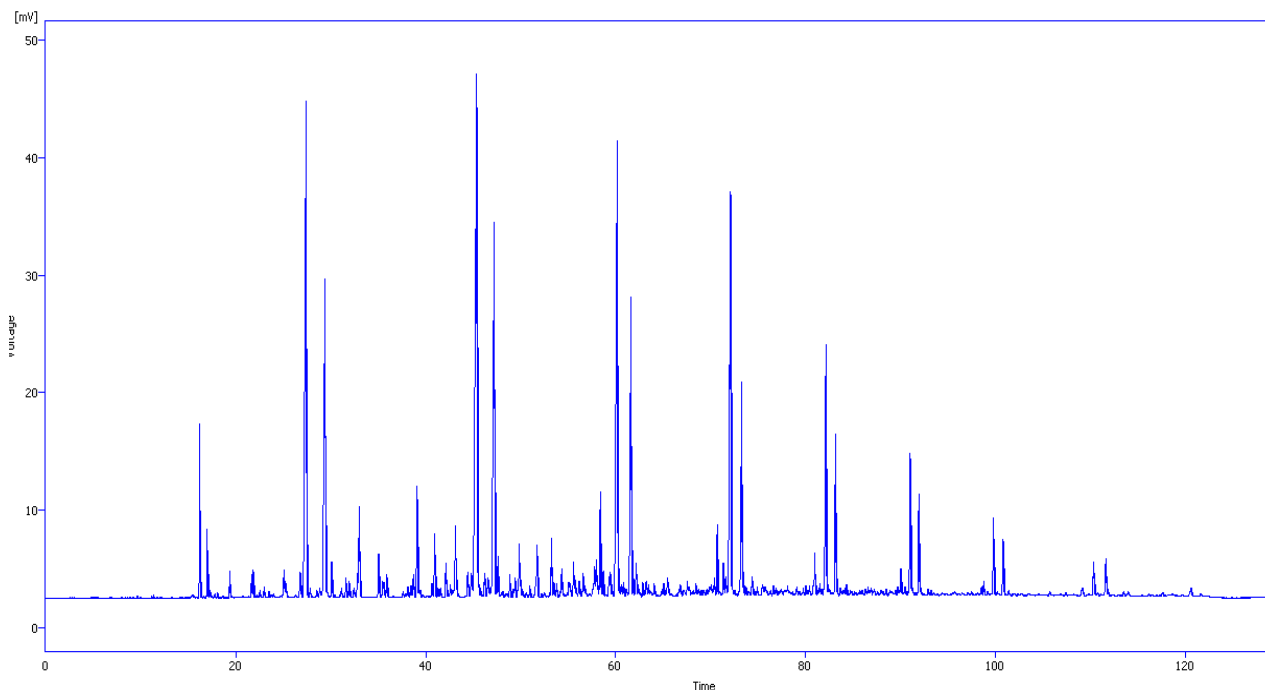


Figure 2. Chromatographic study of the light liquid samples recovered from the hydrolytic depolymerization of the polyethylene mix.

The chromatographic study of the liquid sample recovered from the hydrolytic depolymerization of the polyethylene mix produces different components such as paraffin, iso-paraffin, olefin, aromatic and naphthenes. The analysis was carried out in a PIONA analyzer having 100m capillary DHA column with temperature programming at ramp temperature of 5⁰C /min [6].The different components of the liquid with there proportions is shown in the table 2.The components were observed in the form of peaks and were identified according to there different retention times. The depolymerization of the polyethylene into light liquid component is some what similar to the conventional naphtha component having varying composition. The different components of the light naphtha like components observed were shown in the table 2. In this degradation process the components recovered have higher percentage of olefins components. Paraffinic and iso-paraffinic components were also identified with higher percentage.

Components	Percentage in (%V)
Paraffin	30
Iso-Paraffin	11
Olefin	43
Naphthenes	6
Aromatic	10

Table 2. PIONA analysis of light liquid components recovered from depolymerization of the polyethylene mix.

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This is also evident that the different component so produced may have undergone different reaction mechanism at different conditions.

During the thermal degradation of many polymers, other reactions may take place at the same time as the isomerization, cyclization, aromatization, recombination of species, etc. During the depolymerization process, Methyl-group shift and isomerization of saturated hydrocarbons are some of the important isomerization reactions. The carbonium ion intermediates can undergo rearrangement by hydrogen or carbon-atom shifts leading to a double-bond isomerization of an olefin.

The cyclization reaction is followed by the Diels Alder reaction mechanism, in which the Dienes reacts with the Dienophiles in presence of thermal energy, produces a cyclic ring structure.

The cyclization reactions may occur through the formation of some carbonium ion intermediates. Such as when hybridising abstraction first locates in an olefin at a position several carbons were removed from the double bond, these resulted in the formation of an olefinic carbonium ion. The carbonium ion involve intramolecular attack on the double bond, this will provided a route to cyclization and formation of aromatics.

The variation in the temperature is also one of the factors for the olefinic and aromatic compound formation. Thus each temperature corresponds to a particular time of contact both for olefin formation and aromatization, a certain minimum residence time being required for olefin formation and a certain maximum residence time for aromatization [7].

III. CONCLUSION

The hydroxyrolytic depolymerization of the polyethylene and different types of the polymer shows the formation of the different hydrocarbon components. The reaction mechanism of the different polymers with there straight chain reaction, isomerization reaction, olefinic, cyclic and aromatization reaction conditions polymers were studied in the paper. The chromatographic study of the gaseous components provides the composition of the gases recovered, which can be useful in deriving the liquefied petroleum gases from it. Some amount of the hydrogen and CO₂ were also observed. The PIONA analysis of the light liquid component recovered from the liquid sample provides information about the different components such as paraffin, iso-paraffin, olefin, naphthenic and aromatic components in the sample which is comparable with the conventional naphtha samples.

IV. ACKNOWLEDGEMENT

The author is thankful to Mr. P. K. Rudra , DGM(TS), Mr. A. S. Sarkar, Ex-Deputy Manager, Mr. Bhag Singh, QCO, and Dr. Kajal Ambuj, Barauni Refinery, Indian Oil Corporation Limited for extending there helping hands in completing this paper. The author also acknowledges the contribution of Mr. Ashok Kumar Roy, Assistant General Manager, M-Junction services limited for completing this paper.

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